Theory of Random Degradation and Its Applications to Polymer Modification, Chain Transfer Reactions, and Particle Size Distribution

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A simple computational method to predict the molecular weight distribution (MWD) formed through random chain scission of linear chains is proposed. This method can be applied to any initial MWD including experimentally obtained ones with small computational time. The random degradation theory can be applied to such problems as the effect of chain transfer reactions and the particle size distribution (PSD) formed in microemulsion polymerization, as well as the random degradation of polymer chains.

1. Introduction

Modification of the molecular weight distribution (MWD) through random scission degradation of polymers provides an attractive research field, combining at the same time fundamental and applied topics of great interest. Theoretical description of the random chain scission has been studied for many years by application of the analytical solutions for several representative polymer MWDs[1]-[7] and by using numerical simulation technique, notably through the Monte Carlo (MC) method, for more general cases. [8]-[14]

Compared with the MC technique, the analytical approach is usually easier to use with superior precision. On the other hand, the analytical solution can be obtained only for several limited distribution functions and may not be applied to the experimentally obtained distributions. The MC method is a versatile technique and could be applied to various polymer systems. However, the MC simulation results always involve some amount of error, as long as the sample size is finite, and a long calculation time may be needed for obtaining statistically valid distribution.

As an example, suppose the initial polymer distribution is given by the Schulz-Zimm distribution

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whose weight-based function $W_0(r)$ is given by:

$$W_0(r) = \frac{\sigma^\sigma}{u\Gamma(\sigma)}\left(\frac{r}{u}\right)^\sigma \exp\left(-\frac{\sigma r}{u}\right) \quad (1)$$

where u is the number-average chain length, and σ represents the narrowness of the distribution.

When the linear polymer chains having the Schulz-Zimm distribution is severed randomly with scission probability ϕ, the resulting distribution is given by:[5]

$$W(\zeta,\eta) = \frac{1}{u}\left\{2\zeta\eta + (1-\zeta)\zeta\eta^2 + \frac{1}{\Gamma(\sigma)}\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}(\sigma\zeta)^{\sigma+k}C_k\right\}\exp(-\eta\zeta)$$

$$(2)$$

where $\zeta = r/u$, $\eta = u\phi$, and C_k is defined by:

$$C_k = \frac{(\sigma+k)(\sigma+k+1) - 2(\sigma+k+1)\zeta\eta + (\zeta\eta)^2}{(\sigma+k)(\sigma+k+1)} \quad (3)$$

Figs. 1-3 show the MWD change during random scission process with $\sigma = 1$ (the most probable distribution), 0.1 (a broad initial MWD) and 10 (a narrow initial MWD), respectively. The curves are calculated from Eq. (2), and the symbols are from the MC simulation method proposed earlier.[12]-[14] A total of 2×10^4 polymer molecules were simulated in the MC method. In the figure, the magnitude of ϕu represents the average number of scission points in a chain.

As the scission reaction proceeds, the distribution approaches to the most probable distribution whose polydispersity index ($\overline{P}_w/\overline{P}_n$) is 2. Both Eq. (1) and the MC simulation results agree reasonably well. However,
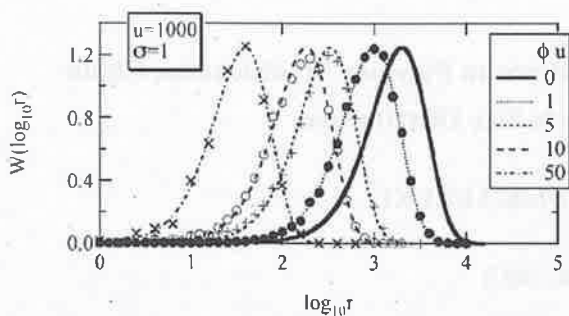
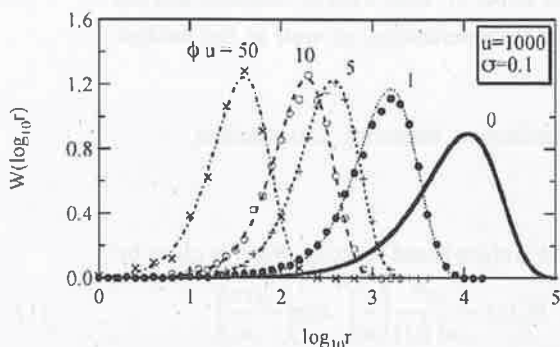Fig. 1 MWD change during random degradation for $u=1000$ and $\sigma=1$.

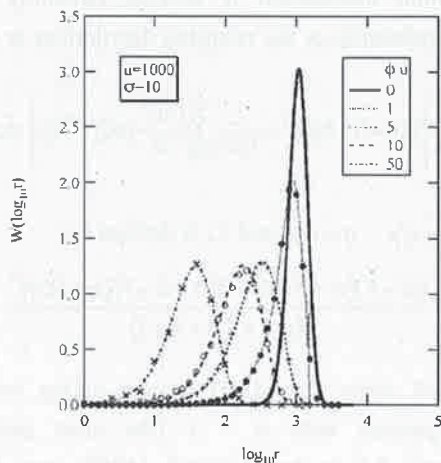Fig. 2 MWD change during random degradation for $u=1000$ and $\sigma=0.1$.

Fig. 3 MWD change during random degradation for $u=1000$ and $\sigma=10$.

with a closer look at these figures, one would notice that (1) the MC simulation results involve small but finite amounts of errors, and (2) the high MW tail of the analytical solution in Fig. 3 with $\phi u =1$ shows an oscillatory behavior, as more clearly shown in Fig. 4. This is because the summation in Eq. (2) involves positive and negative terms that appear alternatively with k. When the magnitude of each term in the summation is

extremely large, it is difficult to obtain the numerical calculation results with high accuracy. Even the analytical solution may not be free from errors when the actual numerical calculation is conducted.

In this article, first, a simple calculation method for the MWD formed through random chain scission is proposed. It is aimed to develop a method that works (1) fast enough (2) with higher precision, and that (3) can be applied to any type of initial MWDs. The equations to calculate the number- and weight-average chain lengths are also proposed. Then, it will be shown that the random degradation theory can be applied to various problems, including seemingly unrelated phenomena. The theory is applied to: (1) the peroxide promoted degradation of polypropyrene, (2) the MWD formed through the conventional free-radical polymerization that involves chain transfer reactions, (3) the effect of monomer transfer reactions in a living/controlled free-radical polymerization, and (4) the prediction of the particle size distribution in microemulsion polymerization.
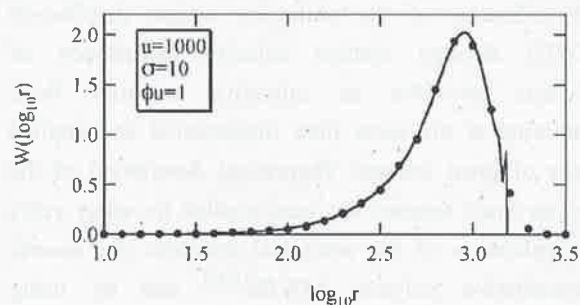

Fig. 4 Closer look at the MWD for $u=1000$, $\sigma=10$ and $\phi u =1$.

2. Theoretical

2.1 Basic Strategy

The fundamental idea proposed in this article is very simple. The MWD formed through random degradation of polydisperse polymers is calculated by superimposing the MWDs formed by random degradation of monodisperse polymers. The solid curve in Fig. 5 shows the initial polymer distribution. Within this initial polymer mixture, the shaded area represents the fraction having a certain chain length. This fraction of polymer would form the polymer represented by the lightly shaded area through random degradation. The whole MWD formed by random chain scission of the initial polymer (represented by the dashed curve) can be

obtained by summing up all of the degraded fractions.

When the initial polymers, whose weight fraction distribution is $W_0(r)$, are degraded by cutting the bonding with probability ϕ, the resulting polymer distribution is represented by:

$$W(r,\phi) = \sum_{s=r}^{\infty} W_0(s) W_{uni}(r,s,\phi) \tag{4}$$

where $W_{uni}(r,s,\phi)$ is the weight fraction distribution formed by random degradation of uniform polymers having chain length s.
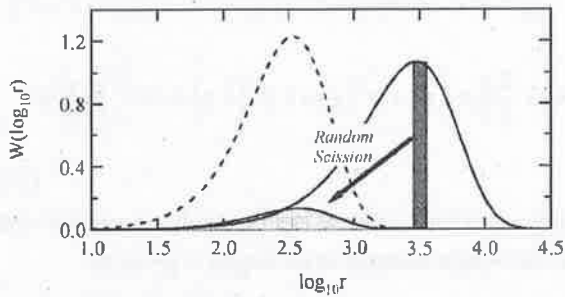

Fig. 5 Fundamental concept of the calculation method for the random degradation of polydisperse polymers.

2.2 Random Degradation of Uniform Polymer Chains

The functional form of the MWD formed by random degradation of uniform polymer chains is already known. However, in this section the full MWD function as well as the weight-average chain length is derived by using the random sampling technique[15] in which only a simple arithmetic calculation is needed. The weight fraction distribution can be obtained by selecting polymer chains on a weight basis. The selection on a weight basis can be conducted by selecting one unit randomly from all units in polymer chains.
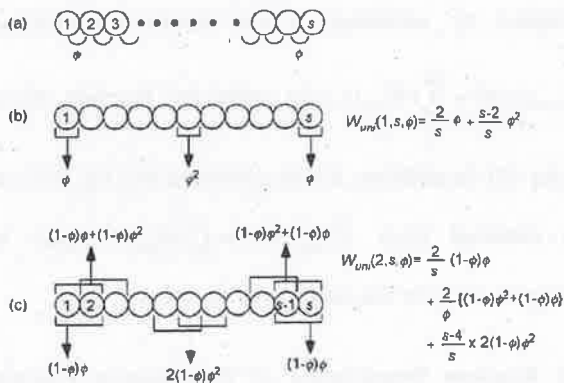

Fig. 6 Derivation of the MWD function formed through random degradation of uniform polymer chains.

Consider a polymer chain having length s as shown in Fig. 6(a). The probability of cutting each bond is ϕ. First, consider the probability of having a chain with length $r = 1$ by selecting one unit randomly, namely, $W_{uni}(1,s,\phi)$. As shown in Fig. 6(b), if one chooses the end units (first or the last unit) whose probability is $2/s$, the chain with $r = 1$ can be obtained by cutting one bond whose probability is ϕ. On the other hand, if one chooses other than the end units whose probability is $(s-2)/s$, two bonds connected to the randomly selected unit must be cut to obtain a chain with $r = 1$ whose probability is ϕ^2. Therefore, $W_{uni}(1,s,\phi)$ is given by:

$$W_{uni}(1,s,\phi) = \frac{2}{s}\phi + \frac{s-2}{s}\phi^2 \tag{5}$$

Similarly, $W_{uni}(2,s,\phi)$ can be determined as follows. (i) If one chooses the end units, the chain with $r = 2$ can be obtained by connecting the neighboring unit while cutting the second bond. The probability of causing such type of events is $(2/s)(1-\phi)\phi$. (ii) If one chooses the second to the end units, the chain with $r = 2$ can be obtained as follows. If the end unit is connected, the other side bonding must be cut. On the other hand, if the counter side from the end is connected, two bonds must be cut, as shown in Fig. 6(c). The probability of causing such type of events is $(2/s)[(1-\phi)\phi+(1-\phi)\phi^2]$. (iii) If one chooses other than the above units whose probability is $(s-4)/s$, two bonds must be cut while connecting one of the neighboring units. Therefore, the probability of causing such events is $[(s-4)/s] \times 2(1-\phi)\phi^2$. $W_{uni}(2,s,\phi)$ can be obtained by summing up the probability for these three types of possible events:

$$W_{uni}(2,s,\phi) = \frac{2}{s}(1-\phi)\phi + \frac{2}{s}\left\{(1-\phi)\phi+(1-\phi)\phi^2\right\} + \frac{2(s-4)}{s}(1-\phi)\phi^2$$

$$= \frac{4}{s}(1-\phi)\phi + \left\{\frac{2}{s}+\frac{2(s-4)}{s}\right\}(1-\phi)\phi^2 \tag{6}$$

The same discussion leads to:

$$W_{uni}(3,s,\phi) = \frac{6}{s}(1-\phi)^2\phi + \left\{\frac{6}{s}+\frac{3(s-6)}{s}\right\}(1-\phi)^2\phi^2 \tag{7}$$

In general, $W_{uni}(r,s,\phi)$ is given by:

$$W_{uni}(r,s,\phi) = \frac{2r}{s}(1-\phi)^{r-1}\phi + \left\{\frac{2}{s}\sum_{i=1}^{r-1}i+\frac{r(s-2r)}{s}\right\}(1-\phi)^{r-1}\phi^2$$

$$= \frac{r\phi}{s}(1-\phi)^{r-1}\left\{2+(s-r-1)\phi\right\} \tag{8}$$

On the other hand, the chains with $r = s$ is obtained only when no bonds are cut, and $W_{uni}(r,s,\phi)=(1-\phi)^{s-1}$. The obtained results are summarized as follows:

$$W_{uni}(r,s,\phi) = \begin{cases} \dfrac{r\phi}{s}(1-\phi)^{r-1}\{2+(s-r-1)\phi\} & (r<s) \\ (1-\phi)^{r-1} & (r=s) \\ 0 & (r>s) \end{cases} \quad (9)$$

For the cases with $\phi \ll 1$ and $r \gg 1$, Eq. (9) can be approximated to:

$$W_{uni}(r,s,\phi) \cong \begin{cases} \dfrac{r\phi}{s}\{2+(s-r)\phi\}\exp(-\phi r) & (r<s) \\ \exp(-\phi r) & (r=s) \\ 0 & (r>s) \end{cases} \quad (10)$$

Equation (10) agrees with the solution obtained by Saito[5] in which the integro-differential equation was used.

The number-average chain length can be obtained simply from the stoichiometric argument. The number-average chain length can always be obtained by taking the ratio between the total number of monomeric units and the total number of polymer molecules. The number of polymer chains increases by one by cutting one bond, and therefore:

$$\overline{P}_n = \frac{1}{\dfrac{1}{\overline{P}_{n,0}}+\left(1-\dfrac{1}{\overline{P}_{n,0}}\right)\phi} = \frac{\overline{P}_{n,0}}{1+\left(\overline{P}_{n,0}-1\right)\phi} \quad (11)$$

where $\overline{P}_n^0$ is the number-average chain length of the original (initial) polymer chains.

The weight-average chain length can be obtained from the distribution function, Eq. (9) or (10). However, in order to show the versatility of the random sampling technique, it is derived by using this technique. Look at Fig. 6(a) again. One chooses one unit randomly, and the expected chain length so selected is the weight-average chain length. To simplify the discussion, let us assume $s = 4$. Suppose one has chosen the first unit. In this case, one unit has already been ensured. The probability that the second unit is connected is $p = 1-\phi$ and if the second unit is connected, the number of units on this chain increases by one. Therefore, the expected number of units up to the second unit is $1+p \times 1$. The probability that the third unit exists in the selected chain is p^2, and the expected number of units up to the third unit is $1+p \times 1+p^2 \times 1$. As a consequence the total expected number of units when the first unit is selected randomly, $\overline{P}_w^{(1)}$ is given by:

$$\overline{P}_w^{(1)} = 1+p+p^2+p^3 \quad (12)$$

Please remember that we are now considering the case

with $s = 4$.

Next, consider the expected weight when the second unit is chosen randomly. Toward the right direction, the expected weight including the selected unit is $1+p+p^2$. Looking toward the left-hand side, the expected weight is $p \times 1$. Therefore, $\overline{P}_w^{(2)}$ is given by:

$$\overline{P}_w^{(2)} = 1+p+p^2+p \quad (13)$$

Any unit on the chain can be selected with equal probability, $1/4$, and therefore, the total expected weight, which is equal to the weight-average chain length of the whole reaction mixture, $\overline{P}_w$ is given by:

$$\begin{aligned} \overline{P}_w &= \frac{1}{4}\left(\overline{P}_w^{(1)}+\overline{P}_w^{(2)}+\overline{P}_w^{(3)}+\overline{P}_w^{(4)}\right) \\ &= \frac{1}{4}\left\{\left(1+p+p^2+p^3\right)+\left(1+p+p^2+p\right)+\left(1+p+p+p^2\right)+\left(1+p+p^2+p^3\right)\right\} \\ &= 1+\frac{2}{4}\left\{\left(p+p^2+p^3\right)+\left(p+p^2\right)+p\right\} = 1+\frac{2}{4}\sum_{j=1}^{3}\sum_{i=1}^{j}p^i \end{aligned}$$

$$(14)$$

In general for the initial uniform polymer chains with $r = s$, the weight-average chain length is given by:

$$\overline{P}_{w,uni}(s,p) = 1+\frac{2}{s}\sum_{j=1}^{s-1}\sum_{i=1}^{j}p^i = 1+\frac{2p}{s}\cdot\frac{s(1-p)+\left(1-p^s\right)}{(1-p)^2}$$

$$(15)$$

By substituting the relationship, $p=1-\phi$, one obtains:

$$\overline{P}_{w,uni}(s,\phi) = 1+\frac{2(1-\phi)}{\phi^2 s}\left\{\phi s-1+\left(1-\phi\right)^s\right\} \quad (16)$$

Equation (16) agrees with the equation developed in ref.[7] in which the cascade theory was used for the derivation.

When $\phi \ll 1$ and $s \gg 1$, Eq. (16) reduces to:

$$\overline{P}_{w,uni}(s,\phi) \cong \frac{2}{\phi^2 s}\left\{\phi s-1+\exp(-\phi s)\right\} \quad (17)$$

Equation (17) agrees with the one derived in ref.[5] in which the integro-differential equation was used to solve. Further, it is straightforward to show that Eq. (16) is obtained by summing up the distribution function,

$$\overline{P}_{w,uni}(s,\phi) = \sum_{r=1}^{s}rW_{uni}(r,s,\phi)$$ using the function shown

in Eq. (9). In addition, it was confirmed that Eq. (17) can

be obtained from $\overline{P}_{w,uni}(s,\phi) = \int_0^s rW_{uni}(r,s,\phi)dr$ by

using Eq. (10) for the distribution function.

2.2 Random Degradation of Polydisperse Polymer Chains

The MWD formed through the random degradation of

polydisperse polymer chains can be obtained from Eq. (4):

$$W(r,\phi) = \sum_{s=r}^{\infty} W_0(s)W_{uni}(r,s,\phi)$$

$$= r\phi(1-\phi)^{r-1} \sum_{s=r+1}^{\infty} W_0(s)\frac{2+(s-r-1)\phi}{s} + W_0(r)(1-\phi)^{r-1} \tag{18}$$

When $\phi \ll 1$ and $s \gg 1$, Eq. (18) reduces to:

$$W(r,\phi) \cong r\phi\exp(-\phi r)\int_r^{\infty} W_0(s)\frac{2+(s-r)\phi}{s}ds + W_0(r)\exp(-\phi r)$$

$$\cong r\phi\exp(-\phi r)\int_r^{r_{max}} W_0(s)\frac{2+(s-r)\phi}{s}ds + W_0(r)\exp(-\phi r) \tag{19}$$

where r_{max} represents the chain length above which $W_0(r)$ practically drops to zero.

Fig. 7 shows the calculated results when the initial polymer distribution follows the Schulz-Zimm distribution with $u=1000$ and $\sigma=10$. As discussed in the introduction part, Eq. (2) has troubles in conducting the numerical calculation, and shows an oscillatory behavior. On the other hand, Eq. (19) shows a nice smooth curve up to the high molecular weight tail that agrees with the MC simulation results. The present method works pretty fast and is free from statistical errors. In addition this method can be applied to any initial polymer distribution including the experimentally obtained ones.

For the number average chain length, Eq. (11) is valid also for the polydisperse systems.

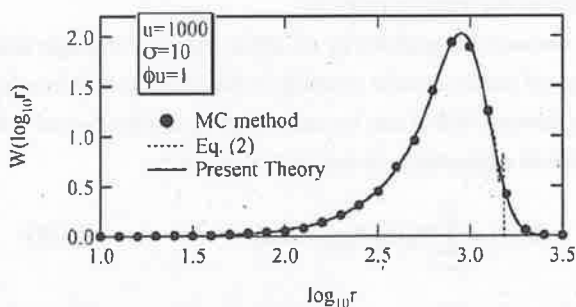The weight-average chain length can be obtained from:

Fig. 7 Calculated MWD formed through random degradation of polymer chains having the Schulz-Zimm distribution with $u=1000$ and $\sigma=10$ when the degree of chain scission is $\phi u = 1$.

$$\overline{P}_w = \sum_{s=1}^{\infty} W_0(s)\overline{P}_{w,uni}(s,\phi)$$

$$= 1 + \frac{2(1-\phi)}{\phi^2} \sum_{s=1}^{\infty} W_0(s)\frac{\phi s - 1 + (1-\phi)^s}{s} \tag{20}$$

For $\phi \ll 1$ and $s \gg 1$, Eq. (20) can be approximated by:

$$\overline{P}_w = \int_0^{\infty} W_0(s)\overline{P}_{w,uni}(s,\phi)ds$$

$$\cong \frac{2}{\phi^2}\int_0^{\infty} W_0(s)\frac{\phi s - 1 + \exp(-\phi s)}{s}ds \tag{21}$$

When the initial polymer distribution $W_0(r)$ follows the Schulz-Zimm distribution represented by Eq. (1), Eq. (20) leads to obtain:

$$\overline{P}_w = 1 + \frac{2(1-\phi)}{u\phi^2}\left\{u\phi - 1 + \left(\frac{\sigma}{\sigma - u\ln(1-\phi)}\right)\right\} \tag{22}$$

Equation (22) agrees with the equation derived in ref.[7]

On the other hand, when Eq. (21) is used, the random degradation of polymers having the Schulz-Zimm distribution leads to:

$$\overline{P}_w = \frac{2}{u\phi^2}\left\{u\phi - 1 + \left(\frac{\sigma}{\sigma + u\phi}\right)^u\right\} \tag{23}$$

Equation (23) agrees with the one developed in ref.[5]

3. Applications

3.1 Polymer Modification by Degradation

The most straightforward application of the present theory is to investigate the modification of polymer distribution by the random chain scission reactions. As an illustration, the experimental data for the peroxide promoted degradation of polypropylene reported in ref.[16] are used. In the present investigation, the main purpose is to show the versatility of the present method; i.e., the present method does not require the MWD represented by some distribution function, but the experimental data that may involve errors could be employed directly. Therefore, we are not going into detailed discussion on the chemistry of this particular reaction system.

The actual reaction mechanism of peroxide promoted degradation of polypropylene could involve complicated reactions; however, it was reported that the random degradation model agrees reasonably well, at least for

the prediction of average molecular weight development during degradation.[16], [17]

The bold curve in Fig. 8 shows the initial polymer distribution. We have taken a set of discrete data from ref.[16] reported graphically. It is expected our numerical data involve some amount of errors because of the graphical read-out method, in addition to the experimental errors. Equation (19) was used to calculate the MWD formed through random chain scission. A spline function was used to interpolate the discrete data for the numerical integration.
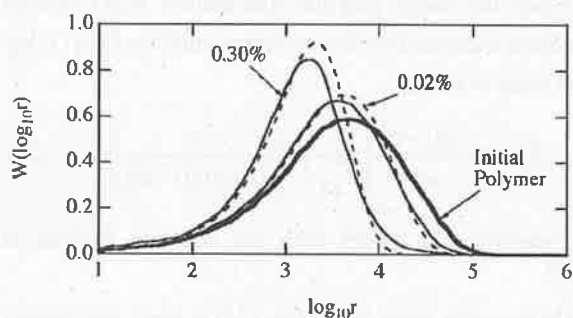

Fig. 8 Peroxide promoted degradation of polypropylene. The solid curves are the experimental data reported in ref.[16], and the dashed curves are the calculated.

In the reported experiment,[16], [17] the initiator, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane was used as a radical generator. The weight percentage of the initiator used is shown in Fig. 8. The ϕ values used are 8×10^{-5} and 5×10^{-4}, respectively for 0.02% and 0.30%. Note that these values were not optimized, and should be regarded as a rough measure of the degree of chain scission. The calculated results agree reasonably well with the experimental data, except for the larger chain length regions.

Up to the present, the average molecular weight data have been mainly used to investigate the polymer degradation. The use of present method promises a more detailed investigation using the full MWD data.

3.2 Chain Transfer Reactions in Conventional Free-Radical Polymerization

In this section, it will be shown that the random degradation theory can be used to investigate the effects of chain transfer reactions, by confirming that the present theory leads to a well-established theoretical MWD function for the conventional free-radical polymerization.

The most probable distribution is the most representative MWD function of synthetic polymers, and the instantaneous MWD (formed within a very small time interval) of free-radical polymerization follows this function when the combination termination reactions can be neglected, which is given by:[18]

$$W_0(r) = r\left(\frac{1}{1+\tau}\right)^{r-1}\left(\frac{\tau}{1+\tau}\right)^2 \qquad (24)$$

$$\tau = \left(R_{td} + \sum_{i=1}^{N} R_{f,i}\right)\bigg/R_p \qquad (25)$$

where R_{td} is the rate of disproportionation termination, R_p is the rate of polymerization, and $R_{f,i}$ represents the rate of chain transfer reaction of type i. It is assumed that there are N types of chain transfer reactions. Therefore, when another type of chain transfer reaction is introduced, τ should be changed to $\tau' = \tau + \xi$ where $\xi = R_{f,N+1}/R_p$. Note that the lifetime of a growing polymer radical is very small, and therefore, the concentration change during such a small time interval can be neglected. The values of τ and τ' are considered constant in the instantaneous MWD.

In the present reaction system, a dead polymer chain is formed either by disproportionation termination or by chain transfer. When an additional chain transfer reaction is introduced, the probability of chain stoppage by this additional transfer reaction is:

$$\phi = \frac{\xi}{1+\tau+\xi} \qquad (26)$$

When chain transfer reaction occurs, a new growing polymer chain is formed at the same time. Therefore, the MWD formed by chain transfer reaction is equivalent to considering chain scission of the polymer molecules without the transfer reaction.

Because the probability of chain stoppage through this type of chain transfer reaction is the same for all bonds, the formed MWD can be calculated by application of the random degradation theory and is given by:

$$W(r) = \sum_{s=r}^{\infty} W_0(s) W_{uni}(r,s,\phi) \qquad (27)$$

By using $W_{uni}(r,s,\phi)$ given by Eq. (9), Eq. (27) leads to:

$$W(r) = \left(\frac{\tau}{1+\tau}\right)^2 r\phi(1-\phi)^{r-1} \sum_{s=r+1}^{\infty} \left(\frac{1}{1+\tau}\right)^{s-1}\{2+(r-s-1)\phi\} + r\left(\frac{1-\phi}{1+\tau}\right)^{r-1}\left(\frac{\tau}{1+\tau}\right)^2$$

$$= r\left(\frac{1-\phi}{1+\tau}\right)^{r-1}\left(\frac{\phi+\tau}{1+\tau}\right)^2 \qquad (28)$$

Substituting ϕ represented by Eq. (26) into Eq. (28),

one obtains:

$$W(r) = r\left(\frac{1}{1+\tau+\xi}\right)^{r-1}\left(\frac{\tau+\xi}{1+\tau+\xi}\right)^2 = r\left(\frac{1}{1+\tau'}\right)^{r-1}\left(\frac{\tau'}{1+\tau'}\right)^2 \quad (29)$$

where $\tau' = \tau + \xi$.

Equation (29) agrees with Eq. (24), which shows that the effect of chain transfer reaction can be investigated by using the present random degradation theory.

When the combination termination is involved, a special consideration is needed for the bonding formed by the combination termination. If this bonding is cut, the fate of the coupled polymer radical by the combination must be considered. To be exact, therefore, the present theory cannot be applied in a straightforward manner. On the other hand, however, the polymer chains normally formed in free-radical polymerization is large, and it is reasonable to neglect the effect of this single bonding on the whole MWD.

When the polymer chain length is large enough, the MWD formed in free-radical polymerization, including the combination termination, is given by the following continuous function:[18]

$$W_0(r) = (\tau+\beta)\left\{\tau+\frac{\beta}{2}(\tau+\beta)r\right\}r\exp\left\{-(\tau+\beta)r\right\} \quad (30)$$

where $\beta = R_{tc}/R_p$ and R_{tc} is the rate of termination by combination.

The probability of chain scission for this case is represented by:

$$\phi = \frac{\xi}{1+\tau+\beta+\xi} \cong \xi \quad (31)$$

Note that we are considering the cases where the formed polymer chains are long enough, and therefore, τ, β, $\xi \ll 1$.

By application of the present theory, the MWD formed with the addition of another transfer reaction would be given by:

$$W(r) = \int_r^\infty W_0(s)W_{uni}(r,s,\phi)ds \quad (32)$$

By using $W_{uni}(r,s,\phi)$ given by the exponential function Eq. (10), one obtains:

$$W(r) = (\tau+\beta)\phi r\exp(-\phi r)\int_r^\infty \left\{\tau+\frac{\beta}{2}(\tau+\beta)s\right\}\left\{2+(s-r)\phi\right\}\exp\left\{-(\tau+\beta)s\right\}ds$$

$$+(\tau+\beta)\left\{\tau+\frac{\beta}{2}(\tau+\beta)r\right\}r\exp\left\{-(\tau+\beta+\phi)r\right\}$$

$$= (\tau+\beta+\xi)\left\{\tau+\xi+\frac{\beta}{2}(\tau+\beta+\xi)r\right\}r\exp\left\{-(\tau+\beta+\xi)r\right\}$$

$$= (\tau'+\beta)\left\{\tau'+\frac{\beta}{2}(\tau'+\beta)r\right\}r\exp\left\{-(\tau'+\beta)r\right\} \quad (33)$$

It is shown here that the present random degradation theory can be applied to investigate the effect of chain transfer reactions on the MWD. The necessary condition is that the rate ratio, $\xi = R_{f,N+1}/R_p$ is kept constant during the formation of a polymer chain, which is valid for the instantaneous MWD in the conventional free-radical polymerization.

If the $(N+1)$th transfer reaction is the monomer transfer, the ξ-value is kept constant during the whole course of polymerization. Therefore, the accumulated MWD can be obtained directly by application of the present theory to the accumulated MWD estimated without monomer transfer reactions as the initial polymer distribution $W_0(s)$.

3.3 Effect of Monomer Transfer Reactions in Living Radical Polymerization

Recently, the controlled/living free-radical polymerization has been significant academic and industrial interest. An important motivation to employ a living free-radical polymerization is to produce polymers having narrow distribution. The frequency of bimolecular termination can be reduced by lowering the active radical concentration, preserving potentially active radicals as dormant. If chain transfer reaction is involved, in general, the ratio R_f/R_p changes along the chain. On the other hand, however, every effort is usually made to reduce the chain transfer reactions by carefully removing potential chain transfer agents from the reaction system. In such cases, the only chain transfer reaction that cannot be prevented is the monomer transfer reaction. For the monomer transfer reaction, $\xi = C_m$, where C_m is the monomer transfer constant, is kept constant during the whole course of chain formation. Therefore, the present random degradation theory can be applied to consider how the monomer transfer reaction broadens the MWD.

As already pointed out,[19] the living radical polymers having very long chain lengths cannot be synthesized because of the monomer transfer reactions. The maximum number-average chain length attainable in any free-radical polymerization is:

$$\overline{P}_{n,max} = 1/C_m \quad (34)$$

The MWD formed in this case is the most probable, and the polydispersity index $(= \overline{P}_w/\overline{P}_n)$ is 2. In order to obtain narrow distribution polymers, the chain length designed to synthesize $\overline{P}_{n,design}$ must be much smaller than $\overline{P}_{n,max}$.

Normally, $C_m \ll 1$, and it is reasonable to set $\phi = C_m$.

The full MWD would be obtained from Eq. (9) or (10) by using the $W_0(r)$ function that does not account the monomer transfer reactions. The number-average chain length can be obtained from Eq. (11), and the weight-average from Eq. (16) or (17).

It was recently shown that the MWD of the ideal living radical polymerization is given by:[20]

$$W_0(r) = (1-p)^2 \, p^{r-1} r e^{-z} F\left[1+r, 2; (1-p)z\right] \quad (35)$$

where z is the average number of active periods during polymerization, and p is the probability of connecting the next unit during the active period that is equal to the rate ratio, $R_p/(R_p + R_D)$ where R_D is the dormant formation rate. In the above equation, it is assumed p is constant during polymerization, and the active periods are distributed randomly. In Eq. (34), $F(a,b;x)$ is the confluent hypergeometric function (Kummer's function of the first kind), represented by:

$$F(a,b;x) = 1 + \frac{ax}{b} + \frac{a(a+1)}{b(b+1)} \cdot \frac{x^2}{2!} + \cdots \quad (36)$$

The MWD formed with the existence of monomer transfer reaction can be calculated from:

$$W(r) \cong C_m r \exp(-C_m r) \int_r^{r_{max}} W_0(s) \frac{\{2 + C_m(s-r)\}}{s} ds + W_0(r) \exp(-C_m r)$$

$$(37)$$

A problem for applying Eq. (37) with the initial MWD given by Eq. (35) is that it may take rather long computational time depending on the calculation conditions because of the complicated hypergeometric function. In such cases, one can resort to a faster calculation method. First, obtain the discrete data points for the initial MWD $W_0(r)$. Then, the continuous approximate function is determined by using, for example, a spline function. Finally, the spline function is used to conduct the integration in Eq. (37).

Some of the examples of the calculated results are shown in ref.[20] It was found that in terms of the weight fraction distribution, the designed number-average chain length $\bar{P}_{n,design}$ should be made smaller than about 10% of $\bar{P}_{n,max}$. On the other hand, however, a significant number of shorter chains are already formed even when $\bar{P}_{n,design}$ is as small as 10% of $\bar{P}_{n,max}$ ($\bar{P}_{n,design} \approx 0.1 \times \bar{P}_{n,max}$). In terms of the number fraction distribution, it may be better to keep $\bar{P}_{n,design}$ smaller than about 5% of $\bar{P}_{n,max}$. If the purpose of using living radical polymerization is to synthesize well-defined block copolymer, it is recommended to keep $\bar{P}_{n,design}$ smaller than about 5% of $\bar{P}_{n,max}$.

Application of the present theory to the initial MWD predicted by the Monte Carlo simulation method can be found in ref.[21]

3.4 Particle Size Distribution (PSD) Formed in Microemulsion Polymerization

In usual microemulsion polymerization, the amounts of monomer and emulsifier initially charged are comparable, and the number of micelles left in the system is much larger than the total number of polymer particles throughout the polymerization.[22] Therefore, the probability of radical entry into the preformed polymer particles is negligibly small. As a simplest model, the microemulsion polymerization can be considered as a polymerization without bimolecular termination.[23], [24] For such a living system, the polymer chain stoppage is dominated by the monomer transfer reactions, without the existence of other chain transfer agents. The polymer particle stops growing when an oligomeric radical formed by the monomer transfer reaction exits from the particle.[24]-[26]

The probability that a growing polymer radical causes the monomer transfer reaction is $C_m/(1+C_m) \cong C_m$. The oligomeric radical (mainly monomeric in most cases) formed by the monomer transfer reaction may then diffuse out of the particle with probability P_{exit}. Therefore, the probability of the radical exit from a growing polymer particle before adding next monomeric unit, ϕ_e is given by:

$$\phi_e = C_m P_{exit} \quad (38)$$

It is expected that P_{exit} is larger for smaller particles, and P_{exit} should be particle-size dependent.[27], [28] On the other hand, it was reported that the model that neglects the size dependency of P_{exit} agrees with experimental data reasonably well,[25] especially when one considers relatively large experimental errors involved in measuring the PSD.

The major objective of the present theoretical investigation is to explore the possibility to synthesize polymer particles with narrow distribution qualitatively, and we use a constant ϕ_e-value in the present investigation. For more detailed investigation, one can resort to the other simulation techniques that account for the nonrandom chain scission, such as the MC simulation method.

Fig. 9 shows the basic concept of the present model microemulsion polymerization system. At $t = t_1$, a radical enters into a micelle, and the particle starts to grow. The

second radical will not enter this particle. The growing polymer chain may be stopped by the monomer transfer reaction, and a new chain may be formed in the particle. The particle continues to grow until the monomeric radical formed by the monomer transfer reaction exits from the particle. Neglecting the bimolecular termination in the water phase for simplicity, the radical that exists from the particle enters into another micelle to generate a new polymer particle. These processes continue until the polymerization is finally stopped at $t = t_R$.
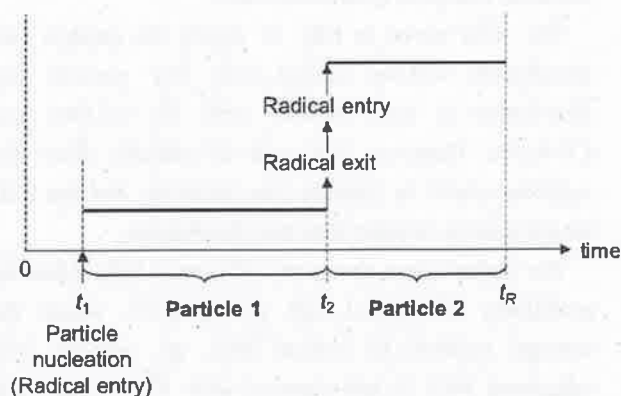

Fig. 9 Schematic representation of the particle formation in a model microemulsion polymerization system.

During the time interval between t_1 and t_R, the total number of monomeric units added to a single radical, i.e., the sum of polymerized monomeric units both in the particle 1 and 2 in Fig. 9, r is given by:

$$r = \int_{t_1}^{t_R} k_p |M|_p \, dt \qquad (39)$$

where $[M]_p$ is the monomer concentration in the polymer particle.

Suppose the weight fraction distribution of polymer particles without the exit of radicals is represented by $W_0(s)$, the weight fraction distribution with the existence of radical exit is given by:

$$W(r) = \int_r^x W_0(s) W_{uni}(r,s,\phi) \, ds$$
$$= \exp(-\phi r) \left\{ \phi r \int_r^x \frac{W_0(s)}{s} [2 + (s-r)] \phi \, ds + W_0(r) \right\} \qquad (40)$$

where $\phi = \phi_e$ given by Eq. (38).

The number fraction distribution, $N(r)$ is therefore given by:

$$N(r) = \frac{\exp(-\phi r)\left\{ \phi \int_r^x N_0(s)[2+(s-r)]\phi \, ds + N_0(r) \right\}}{\int_0^x \exp(-\phi r)\left\{ \phi \int_r^x N_0(s)[2+(s-r)]\phi \, ds + N_0(r) \right\} dr} \qquad (41)$$

First, we are to determine the functional form of $N_0(r)$. Suppose an initiator, whose decomposition rate constant is k_d, is used, the functional form of N_0 when the independent variable is time, t is given by:

$$N_0(t) = \frac{k_d \exp(-k_d t)}{1 - \exp(-k_d t_R)} \qquad (42)$$

Note that $N_0(t)dt$ shows the number fraction of particles generated during the time interval between t and $t+dt$, without the existence of radical exit. From Eq. (39), $N_0(s)$ is given by:

$$N_0(s) = \frac{N_0(t)}{k_p |M|_p} = \frac{N_0(t)}{k_p |M_0|_p (1-x)} \qquad (43)$$

where $[M_0]_p$ is the initial monomer concentration in the monomer-swollen micelles, and x is the monomer conversion to polymer.

For a microemulsion polymerization, it was reported[23], [24] that the following equation describing the conversion of monomer to polymer, x agrees reasonably well with the experimental data, except for a high conversion region:

$$x = 1 - \exp(-\alpha k_d t^2) \qquad (44)$$

where α is a constant defined by:

$$\alpha = \frac{k_p f |M_0|_p |I_0|_w m}{M_0} \qquad (45)$$

In Eq. (45), f is the initiator efficiency, $[I_0]_w$ is the initial initiator concentration in the water phase, m is the molecular weight of monomer, and M_0 is the weight of monomer initially charged per unit volume of water.

Note that any conversion-time relationship, including the experimentally determined equation, can be used in conducting the present theoretical investigation.

The relationship between the particle diameter D_p and the number of monomeric units r is given by:

$$r = \frac{\pi N_{Av} D_p^3 \rho}{6m} \qquad (46)$$

where N_{Av} is Avogadro's number, and ρ is the polymer density.

Illustrative calculations of the PSD: We used the following constants for the illustrative calculations; $\rho = 1 \text{g/cm}^3$, $m = 100$, and $\alpha k_d = 2 \times 10^{-6}$. The solid curve in Fig. 10 shows the conversion development during microemulsion polymerization, calculated from Eq. (44) with $\alpha k_d = 2 \times 10^{-6}$. We set the reaction time, $t_R = 20$min, and the conversion at that time is $x = 0.944$.

The fraction of initiator radicals generated F_{init} is represented by:

$$F_{init} = \frac{N_{I,0} - N_I}{N_{I,0} - N_{I,t_R}} \qquad (47)$$

where N_I is the number of initiator molecules, $N_{I,0}$ is that of the initial value, and N_{I,t_R} is that at $t=t_R$.

The dashed curve in Fig. 10 shows F_{init} when $k_d=1\times10^{-6}\,s^{-1}$. In the present example, because k_d is small, new initiator radicals are generated continuously, resulting in a continuous production of new polymer particles.

The solid curve in Fig. 11 shows the particle size distribution without radical exit when $k_p[M_0]_p=1000\,s^{-1}$. The particle size distribution is broad, with the number average diameter $\overline{D}_p=34.5$nm and the coefficient of variation $CV=42.4\%$. The dashed curve shows the calculated PSD when the probability of radical exit, $\phi=5\times10^{-6}$. In this case, the average number of radical exit, $\phi r_R=3.08$, where r_R is defined by:

$$r_R = \int_0^{t_R} k_p |M|_p dt \qquad (48)$$

Next example is the case with $k_d=1\times10^{-2}\,s^{-1}$ and $N_0(r)$ is broad in the present example, and the PSD with the

existence of radical exit makes the distribution narrower, with $\overline{D}_p=27.8$nm and $CV=39.1\%$. Similar theoretical PSD profiles as Fig. 11 were reported earlier in ref.[29]

$k_p[M_0]_p=200\,s^{-1}$, while the other constants (except for the ϕ-value that will be discussed later) are the same as the previous example. The time development of x and F_{init} for the present case is shown in Fig. 12. The aim of the present example is to examine if small polymer particles with a narrow distribution can be synthesized in microemulsion polymerization. It is obvious that a faster initiation results in a narrower PSD.

The solid curve in Fig. 13 shows the particle size distribution without radical exit. The particle size distribution is very narrow, with $\overline{D}_p=32.0$nm and $CV=6.7\%$. However, the exit of radicals from the particles results in forming new particles, and the PSD would become broader than this distribution.

The dotted curve shows the calculated PSD when the probability of radical exit is $\phi=1\times10^{-6}$, where the average number of radical exit, $\phi r_R=0.123$. The calculated PSD is still narrow, with $\overline{D}_p=30.5$nm and $CV=15.1\%$.
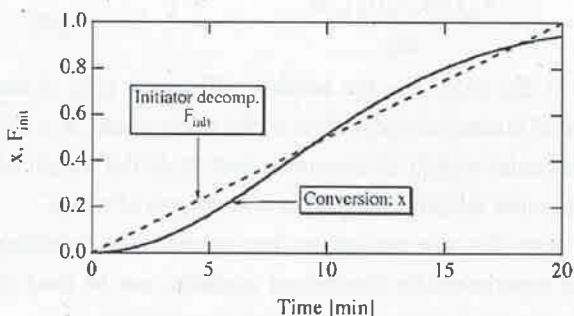
Fig. 10 Conversion (x) and the fraction of initiator radicals generated $(F_{init}$, defined by Eq. (47)) as a function of time, with $\alpha k_d=2\times10^{-6}$ and $k_d=1\times10^{-6}\,s^{-1}$.

Fig.12 Conversion (x) and the fraction of initiator radicals generated (F_{init}) as a function of time, with $k_d=1\times10^{-2}\,s^{-1}$.
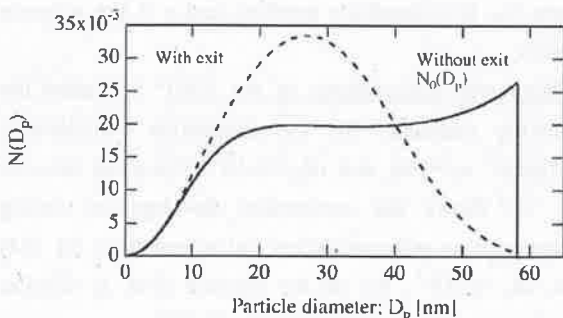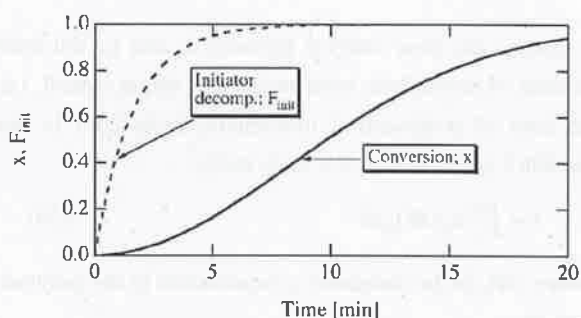
Fig.11 Calculated particle size distribution with and without radical exit for a slow initiator decomposition with $k_d=1\times10^{-6}\,s^{-1}$.
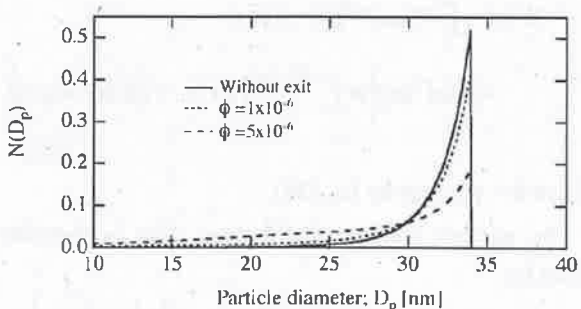
Fig. 13 Calculated particle size distribution with and without radical exit for a fast initiator decomposition with $k_d=1\times10^{-2}\,s^{-1}$.

Obviously, the PSD becomes broader as the ϕ-value increases, and when $\phi = 5 \times 10^{-6}$, the PSD is shown by the dashed line in Fig. 13, with $\overline{D}_p = 26.4$nm and $CV = 26.2\%$.

From the theoretical point of view, the polymer particles with small $\overline{D}_p$ and CV could be produced if (1) the initiation period is short enough compared with the whole reaction time and (2) the polymerization is stopped before the radical exit, namely, by keeping the ϕr_R value small.

4 Conclusions

A simple computational method for the random degradation of linear polymer chains is proposed. This method works fast enough in a usual PC with high precision and can be applied to any type of initial MWD.

In addition to the polymer degradation reactions, the random degradation theory can be applied to various interesting phenomena seemingly no resemblance to the polymer degradation. The theory was applied to the investigation of the effects of chain transfer reactions in both conventional and living free-radical polymerization. For the monomer transfer reactions, the accumulated MWD can directly be predicted by application of the random degradation theory. For living radical polymers, the present theory can be used to determine the designed number-average chain length $\overline{P}_{n,design}$ that are not broadened significantly by the monomer transfer reactions. The $\overline{P}_{n,design}$ value must be significantly smaller than $1/C_m$, where C_m is the monomer transfer constant.

The random degradation theory can also be used to estimate the PSD formed in microemulsion polymerization. It was found that the polymer particles with small $\overline{D}_p$ and CV could be produced under the reaction condition where (1) the initiation period is short enough compared with the polymerization time, and at the same time, (2) the polymerization must be stopped before the particle size grows too large. The number of polymerized monomeric units in a particle must be significantly smaller than $1/\phi_e$, where ϕ_e is the probability of radical exit.

Acknowledgment

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